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(51) International Patent Classification ⁷ : C01F 7/00	A1	(11) International Publication Number: WO 00/44672 (43) International Publication Date: 3 August 2000 (03.08.00)
(21) International Application Number: PCT/EP00/00611 (22) International Filing Date: 27 January 2000 (27.01.00) (30) Priority Data: 60/117,934 29 January 1999 (29.01.99) US (71) Applicant: AKZO NOBEL N.V. [NL/NL]; Velperweg 76, NL-6824 BM Arnhem (NL). (72) Inventors: STAMIREN, Dennis; 6 Rockingham Drive, Newport Beach, CA 92660 (US). BRADY, Mike; 4248 Rhodes Avenue, Studio City, CA 91604 (US). JONES, William; 56 Lantree Crescent, Cambridge CB2 2NJ (GB). (74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel N.V., Intellectual Property Department (Dept AIP), P.O. Box 9300, NL-6800 SB Arnhem (NL).		(81) Designated States: CA, CN, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: PROCESS FOR HYDROTHERMALLY PRODUCING ANIONIC CLAY USING BOEHMITE WHICH HAS BEEN PEPTIZED WITH INORGANIC ACID		
(57) Abstract <p>This patent describes economical and environment-friendly processes for the synthesis of anionic clays. It involves hydrothermally reacting a slurry comprising boehmite which has been peptized with inorganic acid with a magnesium source. There is no necessity to wash or filter the product. It can be spray dried directly to form microspheres or can be extruded to form shaped bodies. The product can be combined with other ingredients in the manufacture of catalysts, absorbents, pharmaceuticals, cosmetics, detergents, and other commodity products that contain anionic clays.</p>		

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PROCESS FOR HYDROTHERMALLY PRODUCING ANIONIC CLAY USING
BOEHMITE WHICH HAS BEEN PEPTIZED WITH INORGANIC ACID

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BACKGROUND OF THE INVENTION

This invention involves the preparation of anionic clays and the preparation of Mg-Al solid solutions by heat-treatment of the anionic clay. Anionic clays have a crystal structure which consists of positively charged layers built up of specific combinations of metal hydroxides between which there are anions and water molecules. Hydrotalcite is an example of a naturally occurring anionic clay, in which carbonate is the predominant anion present. Meixnerite is an anionic clay wherein OH^- is the predominant anion present.

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In hydrotalcite-like anionic clays the brucite-like main layers are built up of octahedra alternating with interlayers in which water molecules and anions, more particularly carbonate ions, are distributed. The interlayers contain anions such as NO_3^- , OH^- , Cl^- , Br^- , I^- , SO_4^{2-} , SiO_3^{2-} , CrO_4^{2-} , BO_3^{2-} , MnO_4^- , HGao_3^{2-} , HVO_4^{2-} , ClO_4^- , BO_3^{2-} , pillaring anions such as $\text{V}_{10}\text{O}_{28}^{6-}$ and $\text{MO}_7\text{O}_{24}^{6-}$, monocarboxylates such as acetate, dicarboxylates such as oxalate, alkyl sulphonates such as laurylsulphonate.

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It should be noted that a variety of terms is used to describe the material which is referred to in this patent as an anionic clay. Hydrotalcite-like and layered double hydroxide are interchangeably used by those skilled in the art. In this patent application we refer to the materials as anionic clays, comprising within that term hydrotalcite-like and layered double hydroxide materials.

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The preparation of anionic clays has been described in many prior art publications.

30

Recently, two major reviews of anionic clay chemistry were published in which the synthesis methods available for anionic clay synthesis have been summarized, F. Cavani et al "Hydrotalcite-type anionic clays: Preparation, Properties and Applications," Catalysis Today, 11 (1991) Elsevier Science Publishers B. V. Amsterdam.

J P Besse and others "Anionic clays:trends in pillary chemistry, its synthesis and microporous solids" (1992), 2, 108, editors: M.I. Occelli, H.E. Robson, Van Nostrand Reinhold, N.Y.

- 10 In these reviews the authors state that a characteristic of anionic clays is that mild calcination at 500 °C results in the formation of a disordered MgO-like product. Said disordered MgO-like product is distinguishable from spinel (which results upon severe calcination) and from anionic clays. In this patent application we refer to said disordered MgO-like materials as Mg-Al solid
- 15 solutions. Furthermore, these Mg-Al solid solutions contain a well-known memory effect whereby the exposure to water of such calcined materials results in the reformation of the anionic clay structure.

For work on anionic clays, reference is given to the following articles:

- 20 Helv. Chim. Acta, 25, 106-137 and 555-569 (1942)
J. Am. Ceram. Soc., 42, no. 3, 121 (1959)
Chemistry Letters (Japan), 843 (1973)
Clays and Clay Minerals, 23, 369 (1975)
Clays and Clay Minerals, 28, 50 (1980)
- 25 Clays and Clay Minerals, 34, 507 (1996)
Materials Chemistry and Physics, 14, 569 (1986).
- In addition there is an extensive amount of patent literature on the use of anionic clays and processes for their preparation.
- 30 European Patent Application 0 536 979 describes a method for introducing pH-

dependent anions into the clay. The clay is prepared by the addition of a solution of $\text{Al}(\text{NO}_3)_3$ and $\text{Mg}(\text{NO}_3)_2$ to a basic solution containing borate anions. The product is then filtered, washed repeatedly with water, and dried overnight. Additionally mixtures of Zn/Mg are used.

5

In US 3,796,792 by Miyata entitled "Composite Metal Hydroxides" a range of materials is prepared into which an extensive range of cations is incorporated, including Sc, La, Th, In, etc. In the examples given solutions of the divalent and trivalent cations are prepared and mixed with base to cause co-precipitation.

10 The resulting products are filtered, washed with water, and dried at 80 °C. Example 1 refers to Mg and Al and Example 2 to Mg and Bi. Other examples are given, and in each case soluble salts are used to make solutions prior to precipitation of the anionic clay at high pH.

15 In US 3,879,523 by Miyata entitled "Composite Metal Hydroxides" also a large number of preparation examples is outlined. The underlying chemistry, however, is again based on the co-precipitation of soluble salts followed by washing and drying. It is important to emphasize that washing is a necessary part of such preparations, because to create a basic environment for co-precipitation of the metal ions a basic solution is needed and this is provided by

20 $\text{NaOH}/\text{Na}_2\text{CO}_3$ solutions. Residual sodium, for example, can have a significant deleterious effect on the subsequent performance of the product as a catalyst or oxide support.

25 In US 3,879,525 (Miyata) very similar procedures are again described.

In US 4,351,814 to Miyata et al. a method for making fibrous hydrotalcites is described. Such materials differ in structure from the normal plate-like morphology. The synthesis again involves soluble salts. For example, an

30 aqueous solution of a mixture of MgCl_2 and CaCl_2 is prepared and suitably

aged. From this a needle-like product $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}$ precipitates. A separate solution of sodium aluminate is then reacted in an autoclave with the solid $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}$ and the product is again filtered, washed with water, and dried.

5

In US 4,458,026 to Reichle, in which heat-treated anionic clays are described as catalysts for aldol condensation reactions, again use is made of magnesium and aluminium nitrate salt solutions. Such solutions being added to a second solution of NaOH and Na_2CO_3 . After precipitation the slurry is filtered and
10 washed twice with distilled water before drying at 125 °C.

15

In US 4,656,156 to Misra the preparation of a novel absorbent based on mixing activated alumina and hydrotalcite is described. The hydrotalcite is made by reacting activated MgO (prepared by activating a magnesium compound such as magnesium carbonate or magnesium hydroxide) with aqueous solutions containing aluminate, carbonate and hydroxyl ions. As an example the solution is made from NaOH, Na_2CO_3 and Al_2O_3 . In particular, the synthesis involves the use of industrial Bayer liquor as the source of Al. The resulting products are washed and filtered before drying at 105 °C.

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In US 4,904,457 to Misra a method is described for producing hydrotalcites in high yield by reacting activated magnesia with an aqueous solution containing aluminate, carbonate, and hydroxyl ions.

25

The methodology is repeated in US 4,656,156.

In US 5,507,980 to Kelkar et al. a process is described for making novel catalysts, catalyst supports, and absorbers comprising synthetic hydrotalcite-like binders. The synthesis of the typical sheet hydrotalcite involves reacting
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pseudo-boehmite to which acetic acid has been added to peptize the pseudo-boehmite. This is then mixed with magnesia. More importantly, the patent summary states clearly that the invention uses mono carboxylic organic acids such as formic, propionic and isobutyric acid. In this patent the conventional approaches to preparing hydrotalcites are presented.

In US 6,539,861 a process is disclosed for preparing a catalysts for synthesis gas production based on hydrotalcites. The method of preparation is again based, on the co-precipitation of soluble salts by mixing with base, for example, by the addition of a solution of RhCl_3 , $\text{Mg}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ to a solution of Na_2CO_3 and NaOH .

Also in US 5,399,537 to Bhattacharyya in the preparation of nickel-containing catalysts based on hydrotalcite use is made of the co-precipitation of soluble magnesium and aluminium salts.

In US 5,591,418 to Bhattacharyya a catalyst for removing sulphur oxides or nitrogen oxides from a gaseous mixture is made by calcining an anionic clay, said anionic clay having been prepared by co-precipitation of a solution of $\text{Mg}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$ and $\text{Ce}(\text{NO}_3)_3$. The product again is filtered and repeatedly washed with de-ionized water.

In US 5,114,898/WO 9110505 Pinnavaia et al. describe layered double hydroxide sorbents for the removal of sulphur oxide(s) from flue gases, which layered double hydroxide is prepared by reacting a solution of Al and Mg nitrates or chlorides with a solution of NaOH and Na_2CO_3 . In US 5,079,203 /WO 9118670 layered double hydroxides intercalated with polyoxo anions are described, with the parent clay being made by co-precipitation techniques.

In US 5,578,286 in the name of Alcoa a process for the preparation of

meixnerite is described. Said meixnerite may be contacted with a dicarboxylate or polycarboxylate anion to form a hydrotalcite-like material. In examples 5-6 hydromagnesite is contacted with pseudoboehmite under high CO₂ pressure to obtain hydrotalcite.

5

In US 4,946,581 and US 4,952,382 to van Broekhoven co-precipitation of soluble salts such as Mg(NO₃)₂ and Al(NO₃)₃ with, and without the incorporation of rare earth salts was used for the preparation of anionic clays as catalyst components and additives. A variety of anions and di- and tri-valent cations are

10 described.

As indicated in the description of the prior art given-above, there are many applications of anionic clays.

These include but are not restricted to: catalysts, adsorbents, drilling muds, catalyst supports and carriers, extenders and applications in the medical field. In particular van Broekhoven has described their use in SO_x abatement chemistry.

Because of this wide variety of large-scale commercial applications for these materials, new processes utilizing alternative inexpensive raw materials are needed to provide a more cost-effective and environmentally compatible processes for making anionic clays. In particular, from the prior art described above one can conclude that the preparation process can be improved in the following ways: the use of cheaper sources of reactants, processes for easier handling of the reactants, so that there is no need for washing or filtration, eliminating the filtration problems associated with these fine-particled materials, the avoidance of alkali metals (which can be particularly disadvantageous for certain catalytic applications): In prior art preparations, organic acids were used to peptize alumina. The use of organic acids is expensive and introduces an additional step in the synthesis process and is therefore not cost-effective.

Further, in drying or calcining the anionic clay prepared by prior art processes gaseous emissions of nitrogen oxides, halogens, sulphur oxides, etc. are encountered which cause environmental pollution problems.

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SUMMARY OF THE INVENTION

Our invention includes processes for producing anionic clays using novel raw materials and utilizing such raw materials in a simple process which involves
10 reacting mixtures with or without stirring in water at hydrothermal conditions. Such processes can be operated in standard laboratory/industrial equipment. More specifically, there is no need for washing or filtering, and a wide range of ratios of Mg/Al in the reaction product is possible.

This invention involves the use of boehmite in aqueous suspensions, where at
15 ambient or elevated temperature magnesium sources, for instance MgO or brucite, are added and the reaction mixture results in the direct formation of an anionic clay. The powder X-ray diffraction pattern (PXRD) suggests that the product is comparable to anionic clays made by other standard methods. The physical and chemical properties of the product are also comparable to those
20 anionic clays made by the other conventional methods. The overall process of this invention is very flexible, enabling a wide variety of anionic clay compositions and anionic clay-like materials involving for example carbonate, hydroxide and other anions to be prepared in an economically and environmental-friendly manner. The process may be carried out in a one step
25 process either in batch or in continuous mode

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1(a) shows a PXRD pattern of commercially available Catapal ®.

30 Figure 1(b) shows a PXRD pattern of commercially available P3 ® alumina.

Figure 1(c) shows a PXRD pattern of commercially available Laroche ® alumina.

Figure 2. shows a PXRD pattern of a commercially available anionic clay.

Figure 3 shows a PXRD pattern of a Mg-Al carbonate anionic clay prepared by
5 coprecipitation.

DETAILED DESCRIPTION OF THE INVENTION

This invention involves the preparation of anionic clays. In particular it describes
10 a process for the preparation of an anionic clay by reacting a slurry comprising boehmite which has been peptized with an inorganic acid and a magnesium source. Said magnesium source may be composed of a solution of a magnesium salt, a solid magnesium-bearing compound or a mixture of the two. Reaction between the Mg source and boehmite results in the direct formation of
15 an anionic clay. Said reaction takes place at hydrothermal conditions. The reaction is preferably carried out under autogeneous conditions. In the method according to the invention carbonate, hydroxyl, or other anions or mixtures thereof, either provided within the reaction medium for example as a soluble salt or absorbed during the synthesis from the atmosphere, are incorporated
20 into the interlayer region as the necessary charge-balancing anion.

Anionic clays prepared by this method exhibit the well known properties and characteristics (e.g. chemical analysis, powder X-ray diffraction pattern, FTIR, thermal decomposition characteristics, surface area, pore volume, and pore
25 size distribution) usually associated with anionic clays prepared by the customary and previously disclosed methods.

Upon being heated, anionic clays generally form Mg-Al solid solutions, and at higher temperatures, spinels. When used as a catalyst, an adsorbent (for
30 instance a SO_x adsorbent for catalytic cracking reactions), or a catalyst support,

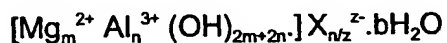
the anionic clay according to the invention is usually heated during preparation and is thus in the Mg-Al solid solution form. During use in an FCC unit, the catalyst or adsorbent is converted from an anionic clay into Mg-Al solid solutions .

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Therefore, the present invention is also directed to a process wherein an anionic clay prepared by the reaction according to the invention, is heat-treated at a temperature between 300 and 1200 °C to form a Mg-Al-containing solid solution and/or spinel.

10

The anionic clay according to the invention has a layered structure corresponding to the general formula



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Wherein m and n have a value such that m/n=1 to 10, preferably 1 to 6, and b has a value in the range of from 0 to 10, generally a value of 2 to 6 and often a value of about 4. X may be CO_3^{2-} , OH^- or any other anion normally present in the interlayers of anionic clays. It is more preferred that m/n should have a

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value of 2 to 4, more particularly a value close to 3.

Since the process disclosed in this patent does not require washing of the product or filtering, there is no filtrate waste or gaseous emissions (e.g. from acid decomposition), making the process particularly environmental-friendly and

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more suited to the environmental constraints which are increasingly imposed on commercial operations. The product can be spray dried directly to form microspheres or can be extruded to form shaped bodies.

Alumina source

The present invention includes the use of boehmite. This includes both boehmites and pseudoboehmites such as Catapal ®, Condea P3 ®, P200 ®, 5 Laroche ® etcetera). In particular we emphasize that there is no need to peptize the boehmite with organic acids. The boehmite is peptized with inorganic acids. These types of acids are not expensive and the use of inorganic acids renders the process cost-effective. Suitable inorganic acids are nitric acid, Hydrochloric acid, sulfuric acid, sulfurous acid, sulfonic acid, 10 phosphoric acid, phosphonic acid, phosphinic acid. Of course mixtures of these acids can be used, and also a mixture of inorganic acid and organic acid can be used. Our invention embodies uses mixtures of boehmites and pseudoboehmites. Also the use of boehmites in mixture with other aluminium sources such as oxides and hydroxides of aluminium, (e.g. sols, aluminium trihydrate, and its thermally treated forms, flash calcined aluminium trihydrate), 15 aluminium salts such as aluminium nitrate, aluminium chloride, aluminium chlorohydrate and sodium aluminate, is envisaged. Said other aluminium sources may be soluble or insoluble in water. Said different aluminium sources may be combined in any sequence in a slurry before and/or after the Mg source 20 is added.

Magnesium source

Mg-bearing sources which may be used include MgO, Mg(OH)₂, magnesium 25 acetate, magnesium formate, magnesium hydroxy acetate, magnesium carbonate, magnesium bicarbonate, magnesium nitrate, magnesium chloride, dolomite, sepiolite. Preferred Mg sources are MgO, Mg(OH)₂, and MgCO₃, because they are cheap, readily available and reactive in the reaction of the present invention. Both solid Mg sources as soluble Mg salts are suitable. Also 30 combinations of Mg sources may be used.

Conditions

5 All that is required is simple hydrothermal treatment of the Mg source and the boehmite in an aqueous suspension. It is possible to purge the slurry with nitrogen or inert gas if an anionic clay with predominantly hydroxide anions are desired, but in general this is not necessary. Thus, the reaction can be conducted in the presence of CO₂. Said CO₂ may be added to the reaction from an outside source.

10

Said aqueous suspension may be obtained by either combining slurries of the starting materials or adding magnesium source to a slurry of boehmite or vice versa. The acid to peptize the boehmite may be added prior to combining the Mg source with the boehmite or the acid may be added to the combined mg
15 source -boehmite slurry. The hydrothermal treatment can be conducted in an autoclave at temperatures above 100 °C and increased pressures. This is particularly advantageous, because it this is faster and a higher conversion is obtained compared to a conventional thermal treatment at atmospheric pressure. Further, larger crystals are obtained when using hydrothermal
20 treatment. There is no need to wash or filter the product, as unwanted ions (e.g. sodium, ammonium, chloride, sulphate) which are frequently encountered when using other preparation methods, are absent in the product.

In a further embodiment of the invention, the process is conducted in a two-step process, e.g. a slurry of boehmite and Mg source is treated thermally at a mild
25 temperature, followed by a hydrothermal treatment. If desired a preformed anionic clay may be added to the reaction mixture. Said preformed clay may be recycled anionic clay from the reaction mixture or anionic clay made separately by the process according to the invention or any other process.

30 Because of its simplicity, this process can be carried out in a continuous mode

by mixing of a first slurry comprising boehmite and a second slurry comprising magnesium source passing the mixed slurry through a reactor vessel which can operate under hydrothermal/autogeneous conditions. Said first and/or second slurry may be subjected to a treatment prior to mixing the slurries.

5

As mentioned-above, if desired inorganic acids and bases, for example for control of the pH, may be added to the slurry before or during reaction or to the individual reactants before combining them in the slurry.

- 10 If desired, the anionic clay prepared by the process according to the invention may be subjected to ion exchange. Upon ion exchange the interlayer charge-balancing anions are replaced with other anions. Said other anions are the ones commonly present in anionic clays and include pillaring anions such as $V_{10}O_{28}^{6-}$, $Mo_7O_{24}^{6-}$. Said ion exchange can be conducted before drying or after
- 15 the anionic clay formed in the slurry.

The process of the invention provides wide flexibility in preparing products with a wide range of Mg:Al ratios. The Mg:Al ratio can vary from 0.1 to 10 , preferably from 1 to 6, more preferred from 2 to 4, and especially preferred to

20 close to 3.

- If an excess of boehmite is used a composition is prepared which contains anionic clay and also unreacted boehmite. In said composition the anionic clay and boehmite are intimately mixed, rather than present as separate phases
- 25 such as in physically mixed mixtures of anionic clay and boehmite. Said composition appears to be highly suitable for use as an additive of as a matrix for catalysts for hydrocarbon conversion. This composition appears especially suitable for sulphur removal from the gasoline and diesel fraction in FCC, SO_x and NO_x removal in FCC, and as a metal trap. The present invention is also
- 30 directed to a composition containing anionic clay and boehmite. Said

composition is obtainable by the process of the invention in which only part of the boehmite is reacted with magnesium source to obtain anionic clay. The rest of the boehmite remains unreacted in the composition.

- 5 On the other hand, also magnesium sources may also be used in excess to obtain a composition containing anionic clay and a magnesium compound, ususally in the form of an oxide or hydroxide. It is even possible to prepare compositions containing anionic clay, boehmite and a magnesium compound with the process according to the invention by controlling the process
- 10 conditions. In said compositions the anionic clay, magnesium compound, and optionally boehmite are intimately mixed, rather than present as separate phases such as in physically mixed mixtures of anionic clay, magnesium compound and boehmite. These compositions appear to be highly suitable for use as an additive or as a matrix for catalysts for hydrocarbon conversion.
- 15 These compositions appear to be especially suitable for use as a metal trap in FCC.

- For some applications it is desirable to have additives, both metals and non-metals, such as rare earth metals, Si, P, B, group VI, group VIII, alkaline earth
- 20 (for instance Ca and Ba) and/or transition metals (for example Mn, Fe, Ti, Zr, Cu, Ni, Zn, Mo, Sn), present. Said metals can easily be deposited on the anionic clay, the solid solution according to the invention, the composition containing anionic clay and boehmite or the composition containing magnesium source, anionic clay and optionally boehmite. They can also be added either to
- 25 the alumina or magnesia source or to the slurry during preparation of the anionic clay.

The present invention is illustrated by the following examples which are not to be considered limitative by any means.

EXAMPLES

COMPARATIVE EXAMPLES BASED ON THE STATE OF THE ART

5 Comparative example 1a

A PXRD pattern was made of Vista Catapal A ®. (Figure 1(a)).

10 Comparative Example 1b

A PXRD pattern was made of Condea Dispersal P3 ® alumina. (Figure 1(b))

Comparative Example 1c

15 A PXRD pattern was made for Laroche Versal 250 ®. (Figure 1(c)).

Comparative Example 2

20 A commercially available sample of anionic clay was obtained from Reheis Corporation ®. Its PXRD pattern is shown in Figure 2.

Comparative Example 3

25 This comparative example illustrates the co-precipitation method where Mg and Al salt solutions are added to a solution of base. (US 3 979 523 Assignee Kyowa Chemical Industry, Japan)

30 A solution containing 0.04 M Of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.08 M Of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 100 ml distilled water was added dropwise and with vigorous stirring to 150 ml of distilled water containing 0.05 M of Na_2CO_3 at room temperature. Mg/Al ratio

of 2.0. The pH was maintained close to 10 by the addition of 3N NaOH and the resulting slurry aged overnight at room temperature. The precipitate was separated by centrifuge, washed several times with hot distilled water then dried at 65 °C overnight.

5

The PXRD pattern obtained from this sample is shown in Figure 3. The results were:

d(A)	7.84	3.90	2.56
I/I ₀	100	40	20

- 10 Thermogravimetric analysis showed three weight losses: at approximately 100, 250 and 450 °C which are ascribed to loss of physisorbed water, interlayer water and loss of CO₂ and lattice dehydroxylation.

EXAMPLES ACCORDING TO THE INVENTION

15

The following examples illustrate the use of Vista Catapal A ® and Condea Disperal P3 ®.

Example 4

20

A slurry of 60.95 g Disperal P3 in 206 g deionized water was mixed in a blender for 5 minutes. The P3 slurry was peptized with HNO₃ (70 wt%) at a pH 1.32 for 15 minutes in a blender. A slurry containing 72.59 g MgO in 109 deionized water was added and blended for 10 minutes. The Mg/Al ratio was 2.3. The pH of the resulting slurry was 8.5. The pH of the final slurry was adjusted to 9.2 with dilute NH₄OH solution resulting in a final slurry solids of 25 wt%. The resulting slurry was heated in a sealed container at 90 °C for 48 hours, and the aged gel was dried overnight at 110 °C. The XRD pattern proved that an

25

anionic clay was formed.

Example 5

- 5 A slurry of 60.95 g Disperal P3 in 206 g deionized water was mixed in a blender for 5 minutes. The P3 slurry was peptized with HNO_3 (70 wt%) at a pH 1.32 for 15 minutes in a blender. A slurry containing 72.59 g MgO in 109 deionized water was added and blended for 10 minutes. The Mg/Al ratio was 2.3. The pH of the resulting slurry was 8.5. The pH of the final slurry was adjusted to 9.2
- 10 with dilute NH_4OH solution resulting in a final slurry solids of 25 wt%. The resulting slurry was heated in a sealed container at 120 °C for 48 hours, and the aged gel was dried overnight at 110 °C. The XRD pattern proved that an anionic clay was formed.

15 Example 6

- A slurry of 50.00 g Catapal A in 204 g deionized water was mixed in a blender for 5 minutes. The Catapal slurry was peptized with HNO_3 (70 wt%) at a pH 3.7 for 15 minutes in a blender. A solution containing 161.5 g magnesium nitrate
- 20 (corresponding with 18.3 wt% MgO) was added and blended for 5 minutes. To this mixture a slurry of 113.2 g MgO in 400 g deionized water was added and mixed for 10 minutes in the blender. The Mg/Al ratio was 5.0. The pH of the resulting slurry was 8.5 with a solids content of 19 wt%. The resulting slurry was heated in a sealed container at 80 °C for 48 hours, and the aged gel was dried
- 25 overnight at 100 °C. The XRD pattern proved that an anionic clay was formed.

Claims:

1. A process for the preparation of anionic clays wherein a slurry comprising boehmite which has been peptized by inorganic acid and magnesium
5 source is hydrothermally treated to obtain an anionic clay.
2. A process according to claim 1 wherein the boehmite is pseudoboehmite .
3. A process according to any one of claims 1-2 wherein the Mg source is MgO
10 and/or Mg CO₃ and/or Mg(OH)₂.
4. A process according to any one of claims 1-3 wherein beside boehmite other alumina sources are present in the slurry.
- 15 5. A process according to any one of claims 1-4 wherein a first slurry comprising boehmite is combined with a second slurry comprising a magnesium source.
6. A process according to claim 5 wherein the process is carried out in a
20 continuous mode.
7. A process according to any one of claims 5-6 wherein metals or non-metals are present in the first and/or the second slurry.
- 25 8. A process according to any one of claims 1-7 wherein the anionic clay is subjected to an ion-exchange treatment.
9. A process according to any one of claims 1-8 wherein the anionic clay is ion
exchanged with pillaring anions such as V₁₀O₂₈⁶⁻ and Mo₇O₂₄⁶⁻.

10. Process according to any one of claims 1-9 wherein metals or non-metals are deposited on the anionic clay.
11. A process according to any one of claims 1-10 wherein metals or non-
5 metals are present in the slurry.
12. A process for the preparation of a Al-Mg-containing solid solution and/or spinel, wherein an anionic clay obtained by any one of the processes of claims 1-12 is subjected to a heat-treatment at a temperature between 300
10 and 1200 °C.
13. A process for the preparation of a composition containing anionic clay and boehmite wherein a slurry comprising boehmite which has been peptized by inorganic acid and magnesium source is hydrothermally treated to obtain a
15 composition comprising anionic clay and boehmite.
14. A composition obtainable by the process of claim 13.
15. A composition containing anionic clay and boehmite in an intimate mixture
20
16. A process for the preparation of a composition containing anionic clay and a magnesium compound wherein a slurry comprising a boehmite and magnesium source is reacted to obtain a composition comprising anionic clay and a magnesium compound
25
17. A composition obtainable by the process according to claim 16.
18. A composition containing anionic clay and a magnesium compound in an intimate mixture.
30

19. A composition containing anionic clay, magnesium compound and boehmite in an intimate mixture.

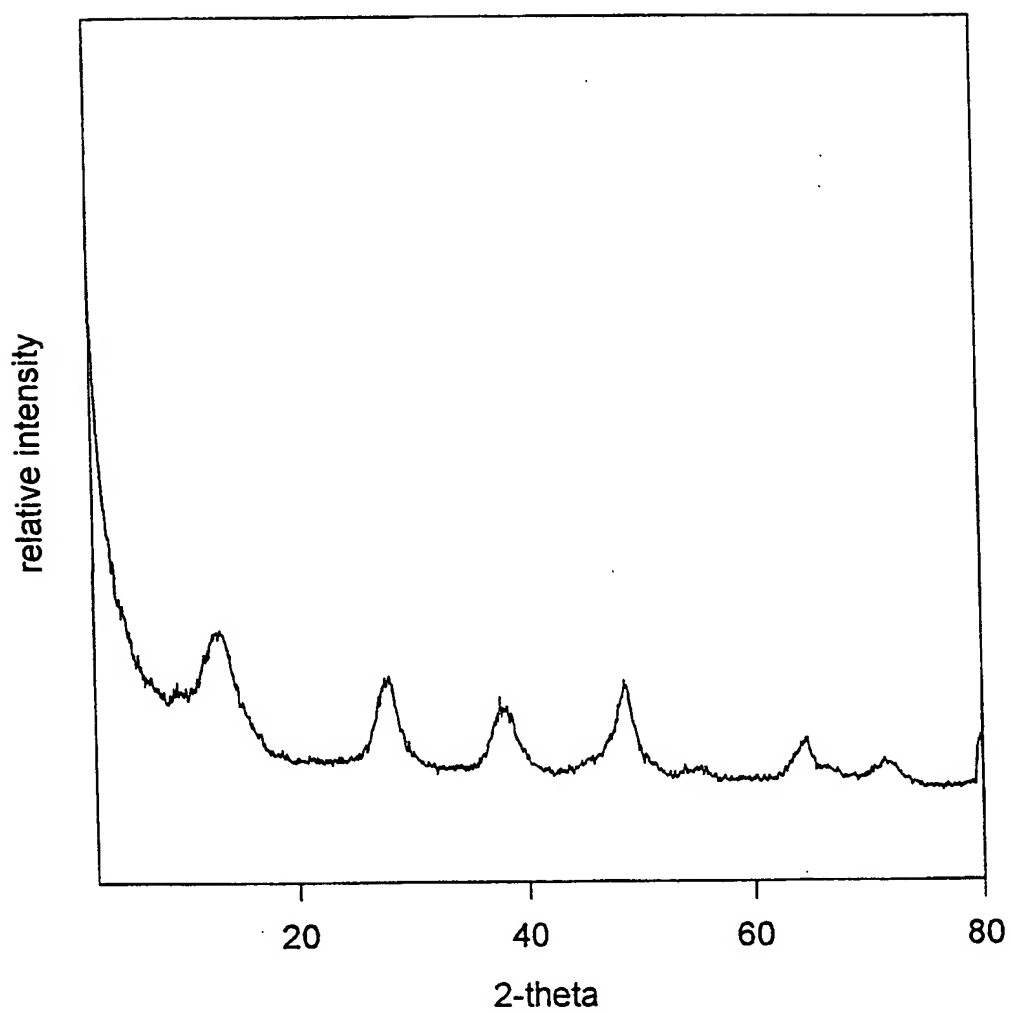
Figure 1(a) Catapal

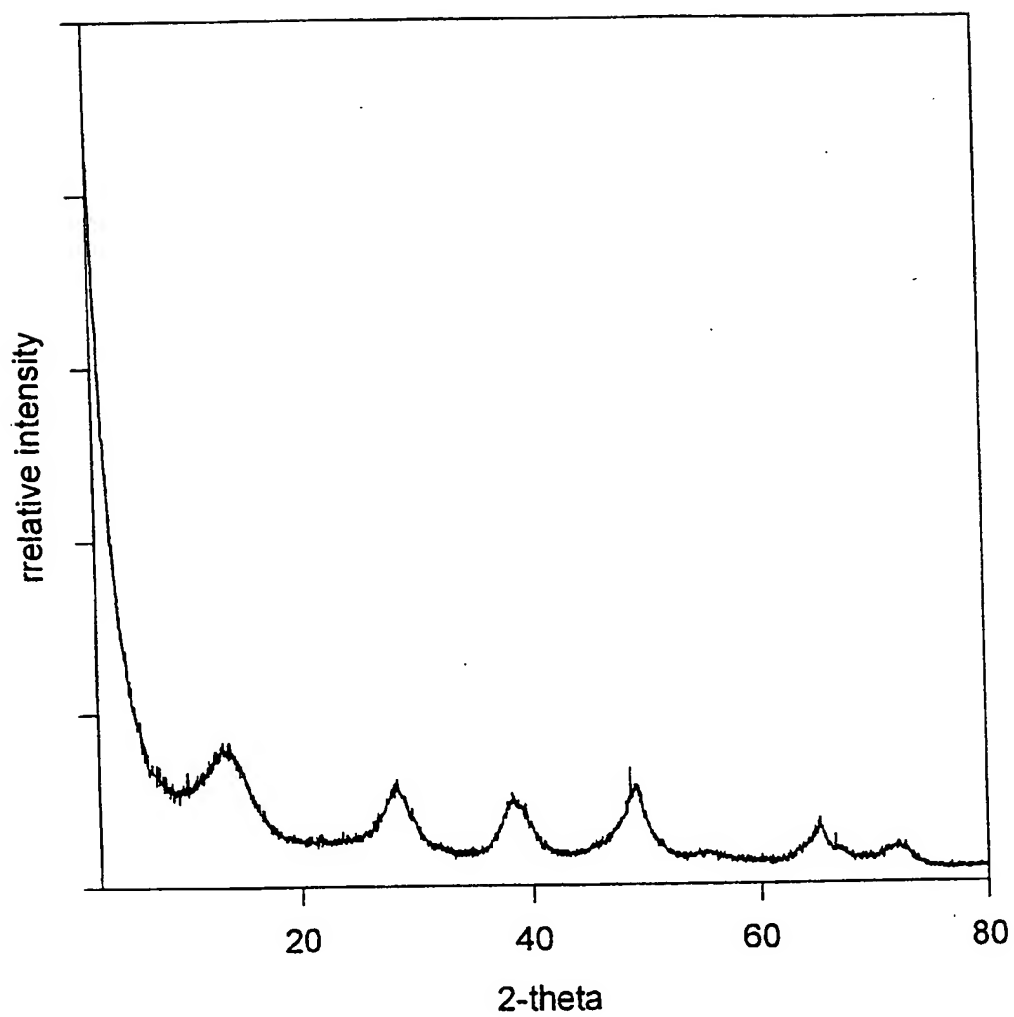
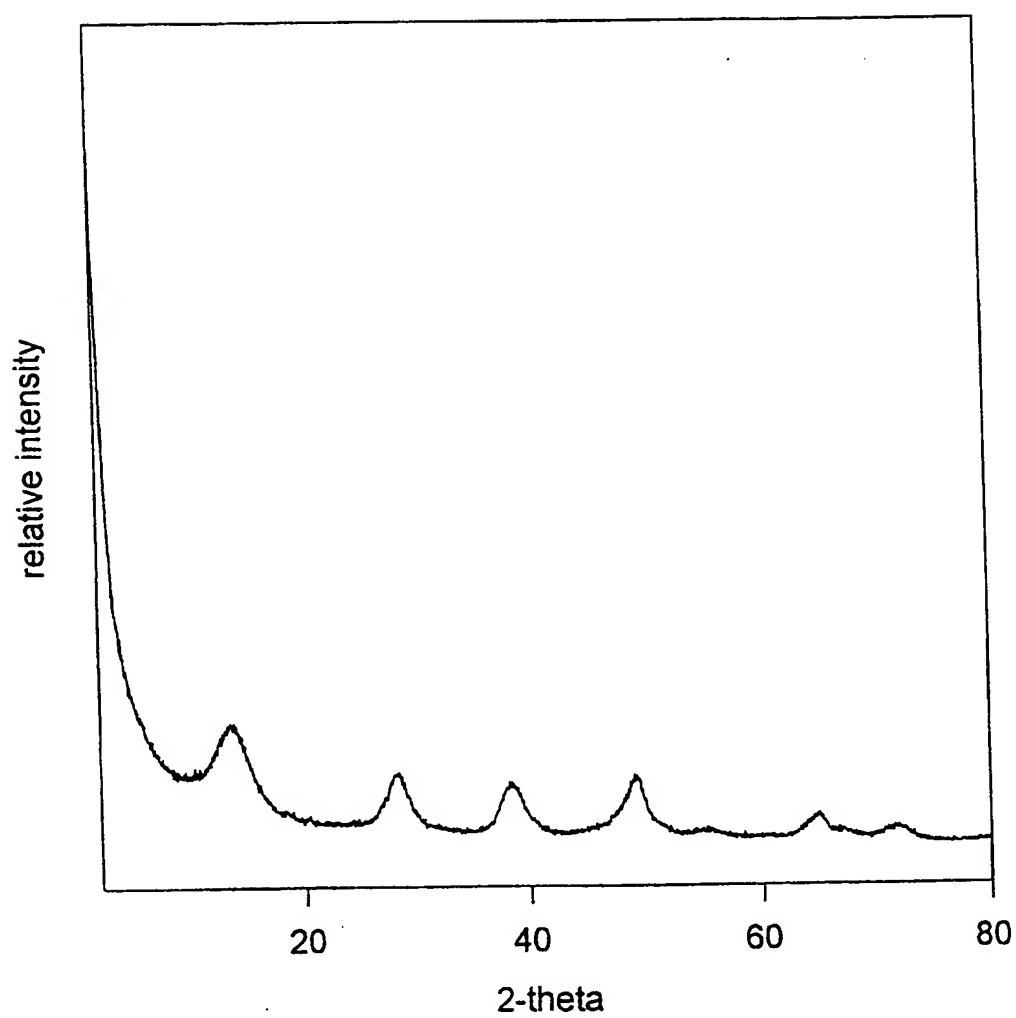
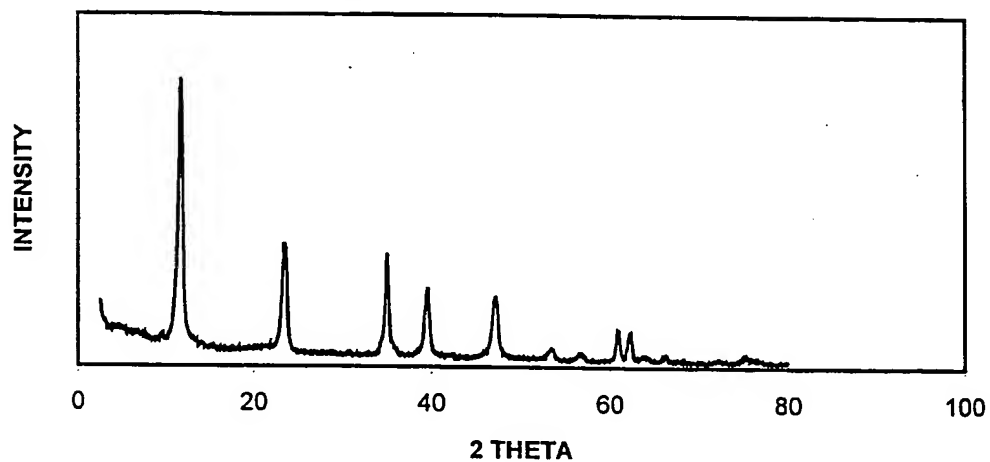
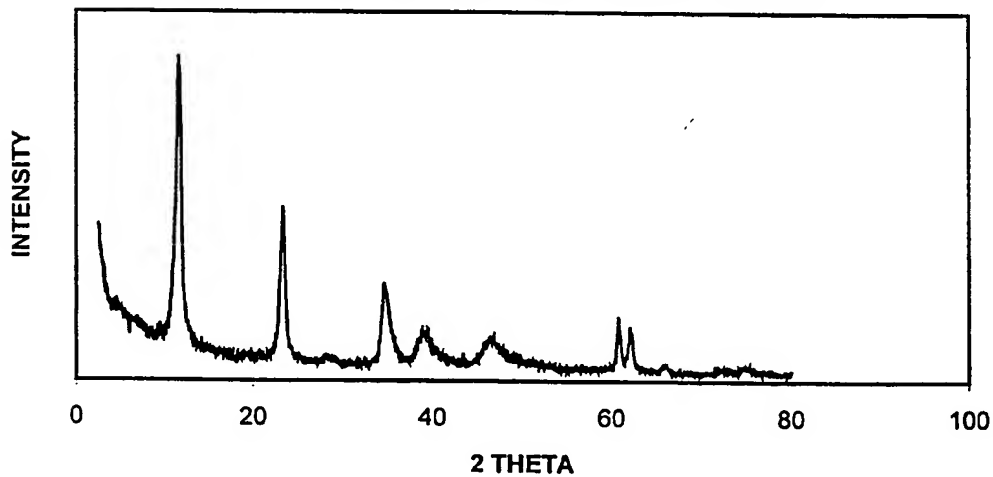
Figure 1(b) P3 alumina

Figure 1(c) Laroche alumina

**FIGURE 2: X-RAY DIFFRACTION PATTERN FOR
COMMERCIAL ANIONIC CLAY**



**FIGURE 3: X-RAY DIFFRACTION PATTERN FOR
ANIONIC CLAY MADE BY CO-PRECIPITATION**



INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/00611

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01F7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 51615 A (ARISTECH CHEMICAL CORP) 19 November 1998 (1998-11-19) the whole document	1-8, 13-19
Y	---	9-12
X	WO 98 03430 A (ARISTECH CHEMICAL CORP) 29 January 1998 (1998-01-29) the whole document	1-10, 12, 17-23
Y	---	9-12
Y	WO 95 21127 A (CHEMSON POLYMER ADDITIVE ;SCHILLER MICHAEL (AT); HENSEL HARTMUT (A) 10 August 1995 (1995-08-10) the whole document	10, 11
Y	EP 0 725 038 A (SNAM PROGETTI) 7 August 1996 (1996-08-07) the whole document	10, 11
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

23 May 2000

Date of mailing of the international search report

31/05/2000

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INTERNATIONAL SEARCH REPORT

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PCT/EP 00/00611

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 774 212 A (DREZDON MARK A) 27 September 1988 (1988-09-27) the whole document	9
Y	US 4 454 244 A (WOLTERMANN GERALD M) 12 June 1984 (1984-06-12) the whole document	9
Y	US 5 426 083 A (BHATTACHARYYA ALAKANANDA ET AL) 20 June 1995 (1995-06-20) the whole document	12
P,X	WO 99 41195 A (AKZO NOBEL NV) 19 August 1999 (1999-08-19) page 11, line 13 - line 18	1,4

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/00611

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9851615 A	19-11-1998	US 5814291 A CA 2259170 A EP 0981497 A	29-09-1998 19-11-1998 01-03-2000
WO 9803430 A	29-01-1998	US 5814291 A	29-09-1998
WO 9521127 A	10-08-1995	AT 401770 B AT 401771 B DE 4439934 A AT 20394 A AT 165795 T AU 683132 B AU 1537395 A CA 2182512 A DE 59502106 D EP 0742782 A ES 2116724 T US 5972245 A AT 20494 A	25-11-1996 25-11-1996 09-05-1996 15-04-1996 15-05-1998 30-10-1997 21-08-1995 10-08-1995 10-06-1998 20-11-1996 16-07-1998 26-10-1999 15-04-1996
EP 0725038 A	07-08-1996	IT MI950184 A	05-08-1996
US 4774212 A	27-09-1988	NONE	
US 4454244 A	12-06-1984	AT 79837 T CA 1209785 A DE 3485888 A DE 3485888 T EP 0131685 A JP 1628367 C JP 2049243 B JP 59207806 A	15-09-1992 19-08-1986 01-10-1992 04-03-1993 23-01-1985 20-12-1991 29-10-1990 26-11-1984
US 5426083 A	20-06-1995	AU 689591 B AU 2596495 A CA 2190745 A EP 0762930 A JP 10501171 T US 5914293 A WO 9532797 A US 5591418 A US 5750020 A US 5843862 A	02-04-1998 21-12-1995 07-12-1995 19-03-1997 03-02-1998 22-06-1999 07-12-1995 07-01-1997 12-05-1998 01-12-1998
WO 9941195 A	19-08-1999	WO 9941197 A WO 9941198 A	19-08-1999 19-08-1999